

A Simple Way for Obtaining the Expression for the Entropy of Fluid

I. The General Consideration

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Abstract

The more simple technique is used to obtain the analytical expression of the entropy for the hard-core fluid in a general case.

Keywords: Entropy, hard-core fluid

In the previous articles [1, 2] was shown how the entropy, S , of an equilibrium square-well (SW) system can be found by integrating the following

thermodynamic relation (hereafter, all thermodynamic quantities are taken per atom):

$$\left(\frac{\partial S}{\partial T}\right)_\rho = \frac{1}{T} \left(\frac{\partial(K+U)}{\partial T}\right)_\rho, \quad (1)$$

where T is the absolute temperature, $K = \frac{3}{2}k_B T$ - kinetic energy, U - potential energy, ρ - mean atomic density, k_B - Boltzmann constant.

Here, we show a more simple way to obtain the entropy of an arbitrary system in a general case at three conditions:

1. The pair-interaction approximation for the potential energy:

$$U = 2\pi\rho \int_0^\infty \varphi(r)g(r)r^2 dr, \quad (2)$$

where $\varphi(r)$ is the pair interatomic potential, $g(r)$ - pair correlation function.

2. The hard-core (HC) model for the pair potential:

$$\varphi_{\text{HC}}(r) = \begin{cases} \infty, & r < \sigma \\ \phi(r), & r \geq \sigma \end{cases}, \quad (3)$$

If $\phi(r) = 0$, we have the hard-sphere (HS) fluid.

3. The following expression for the Fourier transform of the direct correlation function in the HC model, $c_{\text{HC}}(r)$:

$$c_{\text{HC}}(q) = c_{\text{IHC}}(q) - \beta\phi(q), \quad (4)$$

where $c_{\text{IHC}}(q)$ is the Fourier transform of the inside-hard-core (IHC) part of the $c_{\text{HC}}(r)$.

Eq. (4) is true for example in the framework of the mean spherical approximation (MSA) [3] or the random phase approximation (RPA) [4].

From Eq. (4), the structure factor, $a_{\text{HC}}(q)$, is

$$a_{\text{HC}}(q) = \frac{1}{1 - \rho c_{\text{IHC}}(q) + \beta\rho\phi(q)}, \quad (5)$$

where $\beta = (k_B T)^{-1}$.

The difference between entropy of the HS fluid, S_{HS} , and the entropy of the HC fluid, S_{HC} , can be found from eq.(1):

$$S_{\text{HC}} = S_{\text{HS}} + \frac{1}{4\pi^2} \int_0^\infty dq q^2 \phi(q) \int \frac{dT}{T} \left(\frac{\partial a_{\text{HC}}(q)}{\partial T} \right)_\rho = S_{\text{HS}} + \Delta S_{\text{HC}} \quad (7)$$

For cases of RPA [1] and MSA [2] Eq. (7) was being calculated by the straightforward way.

The more simple way to calculate ΔS_{HC} is to perform integrating by parts and to change the variable T on β :

$$\Delta S_{\text{HC}} = \frac{k_{\text{B}}}{4\pi^2} \int_0^\infty dq q^2 \phi(q) \int d\beta \beta \frac{\partial a_{\text{HC}}(q)}{\partial \beta} = \frac{k_{\text{B}}}{4\pi^2} \int_0^\infty dq q^2 \phi(q) \left[\beta a_{\text{HC}}(q) + \frac{\ln a_{\text{HC}}(q)}{\rho \phi(q)} + C \right] \quad (8)$$

The integration constant is being obtained from the condition that $S_{\text{HC}} = S_{\text{HS}}$ at $a_{\text{HC}}(q) = a_{\text{HS}}(q)$:

$$C = -\frac{1}{\rho \phi(q)} \ln a_{\text{HS}}(q) \quad . \quad (9)$$

Eq. (8) can be simplified and the final expression is

$$S_{\text{HC}} = S_{\text{HS}} + \frac{k_{\text{B}}}{4\pi^2} \int_0^\infty dq q^2 \left(\beta a_{\text{HC}}(q) \phi(q) + \frac{1}{\rho} \ln \frac{a_{\text{HC}}(q)}{a_{\text{HS}}(q)} \right) \quad (10)$$

Eq.(10) can be used if the expression for $a_{\text{HC}}(q)$ is known. In the future, the method introduced here will be extended to binary mixtures.

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